Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information for:

Intramolecular Hydrogen Bonding Stabilizes the Nuclearity of Complexes. A comparative study based on the H-carborane and Me-carborane framework.

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Figure S5. ^{1}H{^{11}B}-NMR of compound **3** in d_6-acetone at 260K.

Figure S6. ^{1}H{^{11}B}-NMR and ^{1}H-NMR of compound **3** in d_6-acetone at 298K.

Table S1. Crystal Data for X-ray structures of **1-5.**

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{20}H_{60}B_{40}O_{10}Cu_2$	$C_{22}H_{54}B_{40}N_2O_8Cu_2$	$C_{24}H_{52}B_{40}F_6N_2O_8Cu_2$	$C_{24}H_{60}B_{40}N_2O_9Cu_2$	$C_{20}H_{40}B_{20}N_2O_4Cu$
Formula weight	1020.26	1034.15	1170.16	1080.22	652.28
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	*P* 21/c	*P-21/c*1	*P-21/c*1	*C2/C*	*P-1*
a [Å]	10.318(12)	10.439(18)	22.168(14)	25.36(2)	7.1845(19)
b [Å]	13.473(16)	13.510(2)	12.368(8)	20.832(17)	10.920(3)
c [Å]	22.1272(19)	22.149(3)	22.299(14)	12.538(11)	12.489(3)
α [°]	90	90	90	90	70.332(4)
β [°]	117.26(4)	117.38(6)	101.86(10)	106.308(13)	83.340(4)
γ [°]	90	90	90	90	71.536(4)
V [$Å^3$]	2734(5)	2773.8(7)	5980.6(7)	6357(9)	875.1(4)
Formula Units/Cell	2	2	4	4	1
$\rho_{calc.}$ [g cm^{-3}]	1.239	1.238	1.300	1.129	1.238
μ [mm^{-1}]	0.820	0.808	0.772	0.709	0.655
$R1$[a], [I > 2σ(I)]	0.0569	0.0920	0.0586	0.0699	0.0424
wR_2[b] [all data]	0.1799	0.3179	0.1907	0.2408	0.1131

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$

[b] $wR_2 = [\Sigma\{w(F_o^2-F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{½}$,where $w = 1/[\sigma^2(Fo^2) + (0.0042P)^2]$ and $P=(F_o^2+2F_c^2)/3$

Table S2. Crystal Data for X-ray structures of **2’**and **4’**.

	2'	**4'**
Empirical formula	$C_{32}H_{64}B_{40}O_8N_4Cu_2$	$C_{36}H_{68}B_{40}O_8N_4Cu_2$
Formula weight	1192.35	1244.42
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P-1*
a [Å]	11.764(3)	13.360(8)
b [Å]	13.327(3)	13.632(8)
c [Å]	13.366(3)	24.431(14)
α [º]	99.539(3)	76.585(10)
β [º]	115.311(3)	75.857(9)
γ [º]	112.975(3)	60.941(9)
V [$Å^3$]	1598.8(6)	3738(4)
Formula Units/Cell	1	2
$\rho_{calc.}$ [g cm^{-3}]	1.238	1.106
μ [mm^{-1}]	0.711	0.611
*R*1[a], [I > 2σ(I)]	0.1312	0.0622
wR_2[b] [all data]	0.4576	0.2052

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$

[b] $wR_2 = [\Sigma\{w(F_o^2-F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{½}$,where $w = 1/[\sigma^2(Fo^2) + (0.0042P)^2]$ and $P=(F_o^2+2F_c^2)/3$

Table S3. Selected bond lengths (Å) and angles (˚) for complexes **2’** and **4’**.

	2’	**4’**	
Cu(1)-O(1)	1.954(4)	1.964(19)	Cu(1)-O(1)
Cu(1)-O(2)#1	2.288(5)	2.382(2)	Cu(1)-O(1)#1
Cu(1)-O(5)	1.977(5)	1.993(19)	Cu(1)-O(3)
Cu(1)-N(1)	2.013(8)	2.006(3)	Cu(1)-O(3)#1
Cu(1)-N(2)	2.017(8)	2.011(3)	O(1)-Cu(1)-O(1)#1
Cu(1)-Z			O(3)-Cu(1)-O(3)#1
O(1)-Cu(1)-Y			O(3)-Cu(1)-O(1)#1
O(1)-Cu(1)-O(5)	164.1(2)	163.89(8)	O(3)#1-Cu(1)-O(1)
O(1)-Cu(1)-N(1)	88.3(2)	88.57(10)	O(3)-Cu(1)-O(1)
O(5)-Cu(1)-N(1)	88.1(2)	90.07(10)	O(3)#1-Cu(1)-O(1)#1
O(1)-Cu(1)-N(2)	89.2(2)	89.57(10)	
O(5)-Cu(1)-N(2)	92.0(2)	90.94(10)	
N(1)-Cu(1)-N(2)	170.7(2)	176.68(9)	
O(1)-Cu(1)-O(2)#1	109.93(19)	115.31(7)	
O(5)-Cu(1)-O(2)#1	85.72(18)	80.73(7)	
N(1)-Cu(1)-O(2)#1	92.8(2)	89.61(9)	
N(2)-Cu(1)-O(2)#1	96.5(2)	93.68(8)	

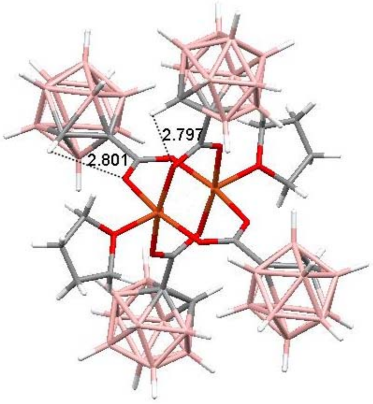
Table S4. Comparison of the structural parameters in Cu(II) dinuclear paddle-wheel and Cu(II) mononuclear carboranylcarboxylate complexes of the ligands 1-CO_2H-2-H-1,2-*closo*-$C_2B_{10}H_{10}$ and 1-CO_2H-2-CH_3-1,2-*closo*-$C_2B_{10}H_{10}$.

	1		**2**		**3**		**4**		**5**		
	C-CH_3	**C-H**	**C-CH_3**	**C-H**	**C-CH_3**	**C-H**	**C-CH_3**	**C-H**		**C-CH_3**	**C-H**
Cu(1)-O(1)	1.956(2)	1.959(2)	1.953(3)	1.962(4)	1.965(3)	1.986(2) 1.941(2)	1.970(3)	1.922(4)	Cu(1)-O(1)	1.9418(16)	1.9409(14)
Cu(1)-O(2)#1	1.959(2)	1.960(2)	1.956(3)	1.957(4)	1.975(3)	1.973(2) 1.952(2)	1.964(3)	1.913(3)	Cu(1)-O(1)#	1.9418(16)	1.9409(14)
Cu(1)-O(3)	1.972(2)	1.959(2)	1.957(3)	1.972(4)	1.971(4)	1.953(2) 1.965(2)	1.965(4)	2.139(4)	Cu(1)-N(1)	2.0222(19)	2.0288(16)
Cu(1)-O(4)	1.973(2)	1.960(2)	1.956(3)	1.967(4)	1.965(3)	1.959(2) 1.977(2)	1.970(4)	2.040(4)	Cu(1)-N(1)#	2.0222(19)	2.0288(16)
Cu(1)-X	2.114(2)	2.100(2)	2.104(3)	2.113(3)	2.118(3)	2.126(2) 2.127(2)	2.104(4)	2.060(5)			
Cu(1)-Cu(1)#	2.672(2)	2.6786(6)	2.693(9)	2.730(12)	2.733(15)	2.7439(5)	2.716(13)	3.009(2)			
C(1)-C(2)OO^-	1.54(1)	1.521(4)	1.518(6)	1.561(6)	1.492(7)	1.500(4)	1.523(6)	1.516(7)		1.538(3)	1.530(3)
C(4)-C(5)OO^-	1.512(1)	1.506(3)	1.514(4)	1.52(1)	1.512(9)	1.530(4)	1.520(9)	1.514(8)			
C(7)-C(8)OO^-						1.504(4)					
C(10)-C(11)OO^-						1.511(4)					

Table S5. Hydrogen bonding C_c-H···O distances (Å) for complexes **1- 5**.

C_c-H_{xA}-O_x	**1**	**2**	**3**	**4**	**5**	**2’**	**4’**
C_3-H_{3A}-O_x	2.797 (x=1)	2.772 (x=2)	3.181 (x=1)	2.750 (x=1)	2.529(x=2)	2.279 (x=5), 2.534 (X=2)	
C_6-H_{6A}-O_X	2.801 (x=3)	3.068 (x=6)	2.665 (x=3)	2.855 (x=3)			2.375(X=5), 2.626(X=2)
C_9-H_{9A}-O_5			2.376				
C_{12}-H_{12A}-O_8			2.597				

For compounds 1-5.



For compounds 2’ and 4’.

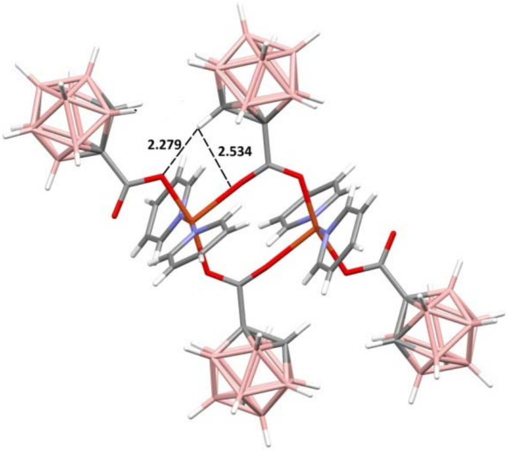


Figure S1. Cyclic voltammetry recorded for complexes 2-5 in acetonitrile

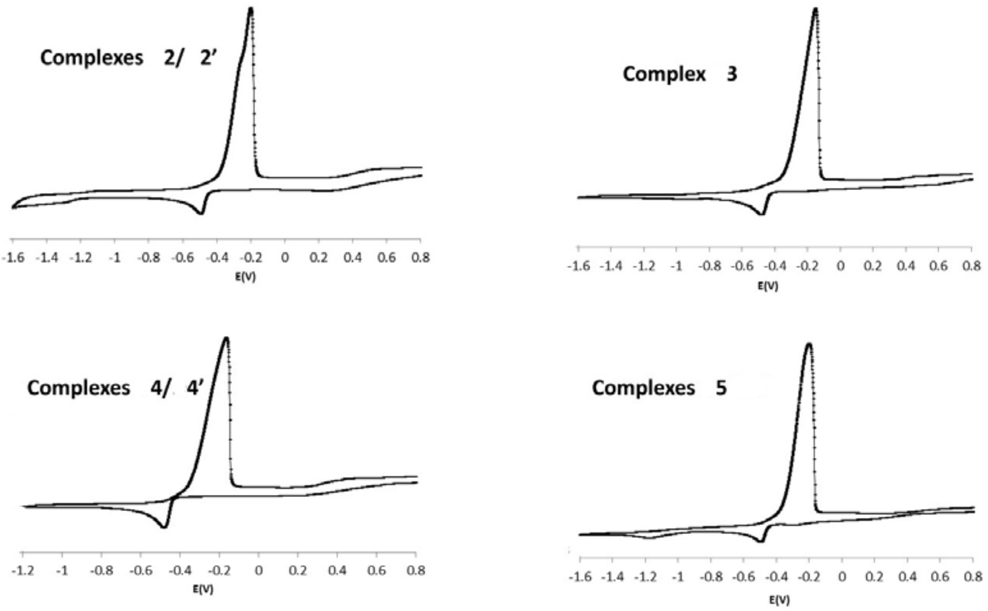


Figure S2. DPV images for complexes **3-5** at potential range from -0.6 to -0.1 in acetonitrile (0.1 M TBAH) with pulse amplitude of 0.05 V, pulse width of 0.05 s, sampling width of 0.02 s and pulse period of 0.5 s.

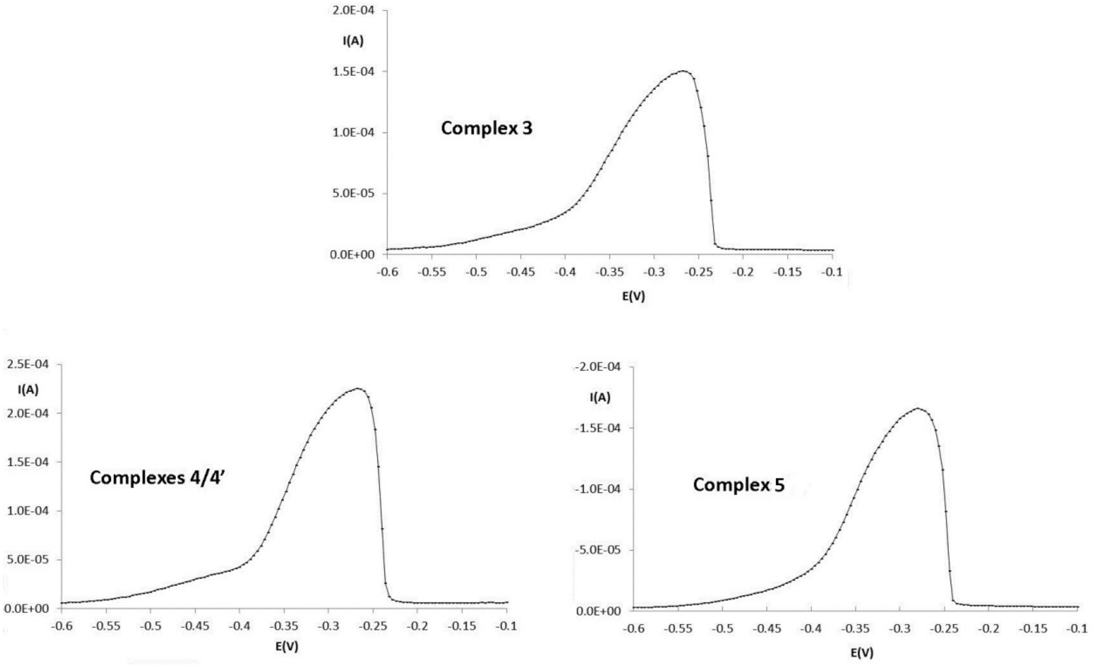
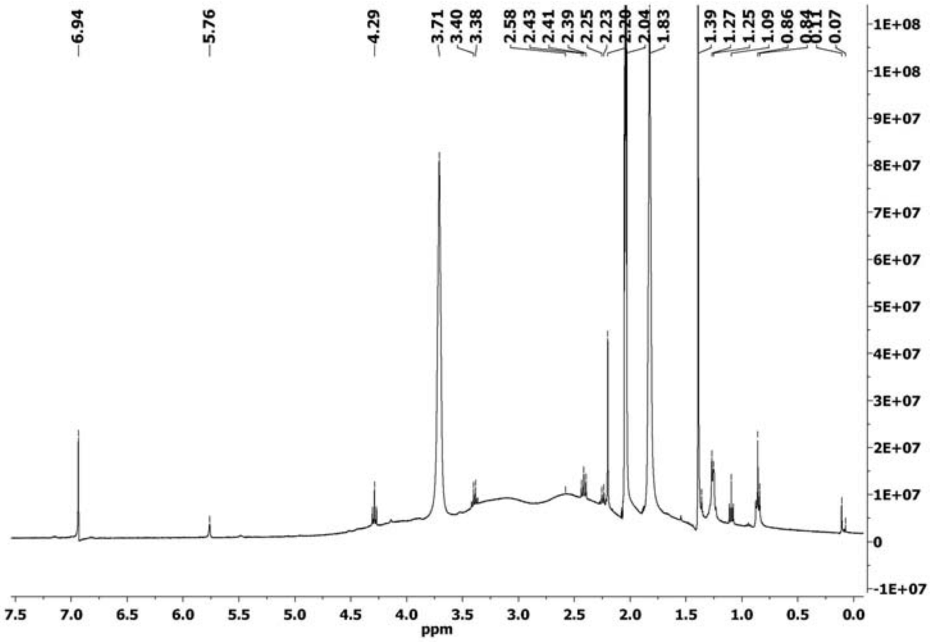


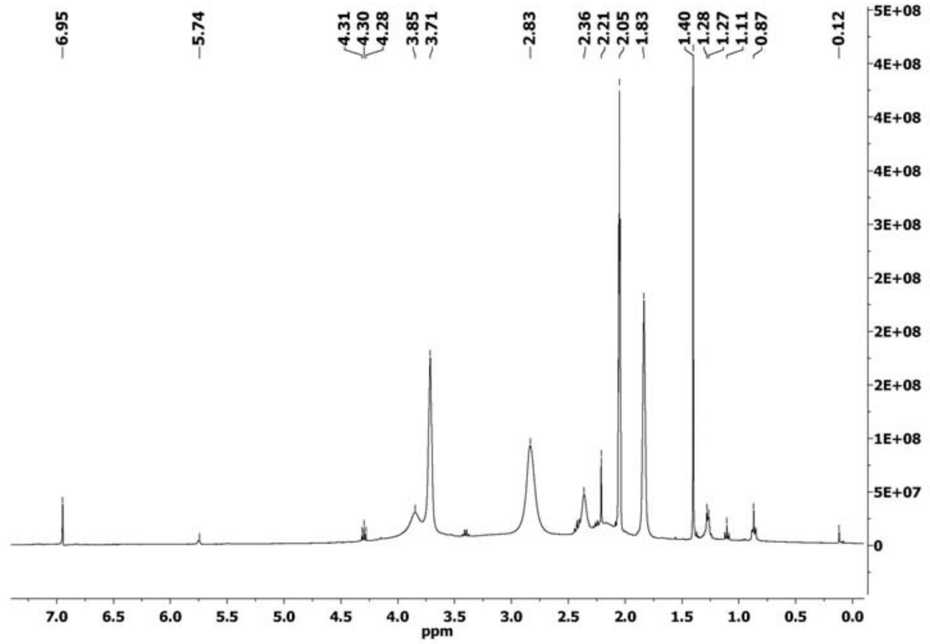
Figure S3. NMR spectra of the compounds **1**, **2/2’**, **3**, **4/4’**, **5** and **LH**.

a) Compound **1**

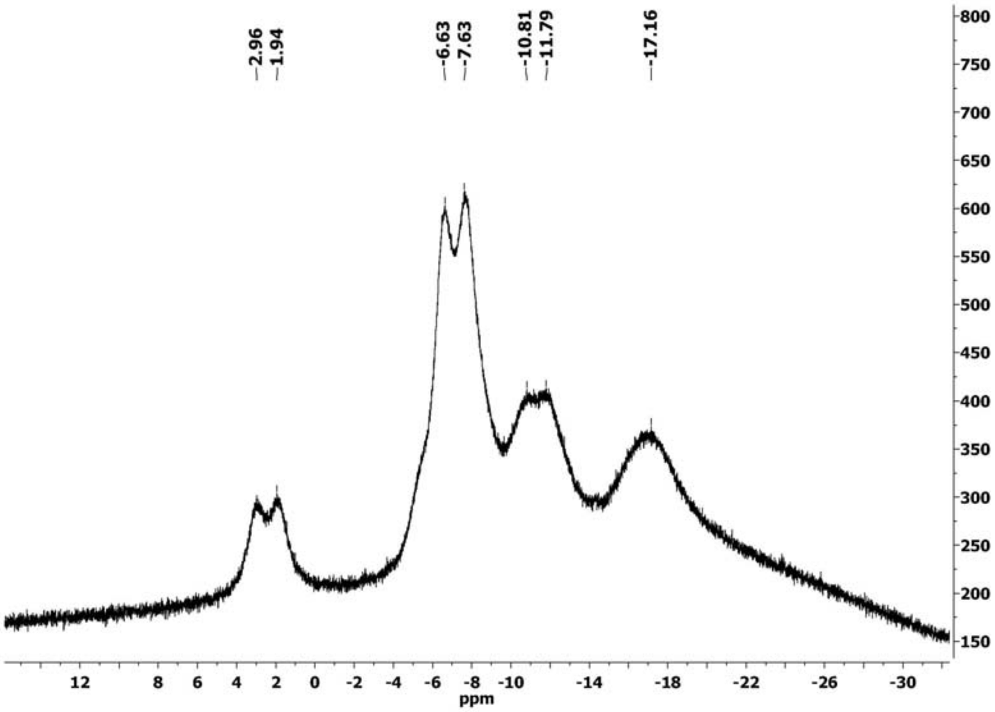
^{1}H-NMR



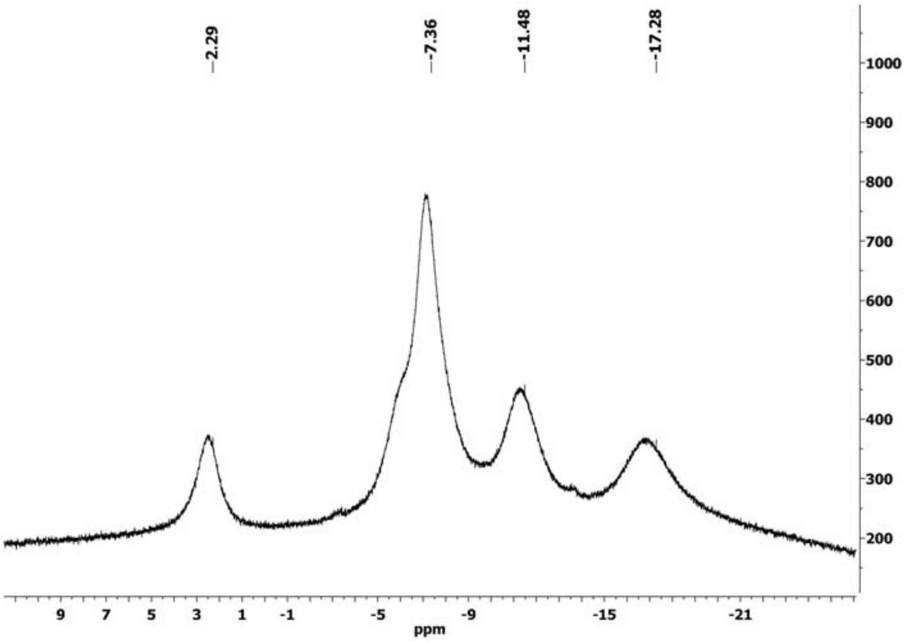
^{1}H{^{11}B}-NMR



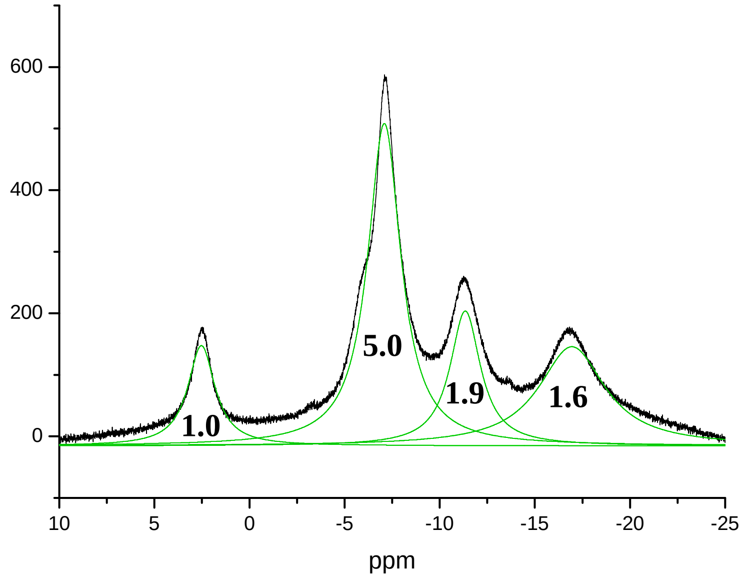
^{11}B-NMR



^{11}B{^{1}H}-NMR

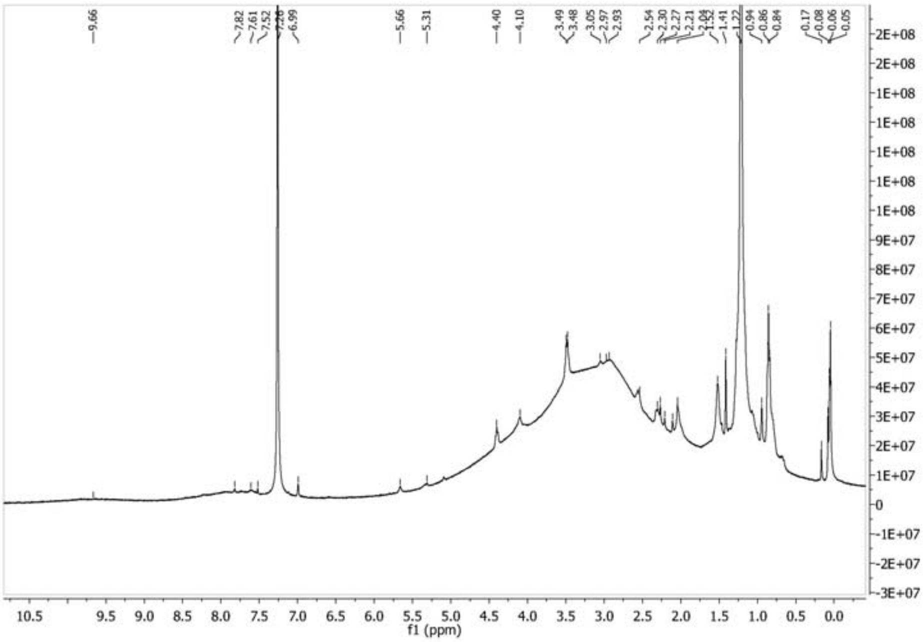


Deconvolution of the ^{11}B NMR spectrum.

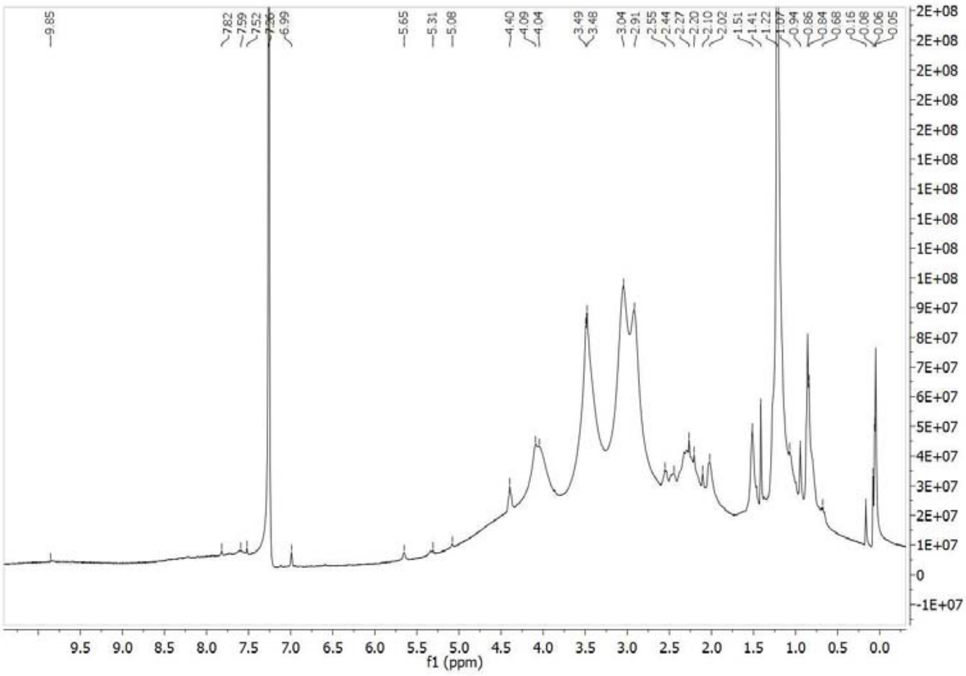


b) Compound **2/2‘**

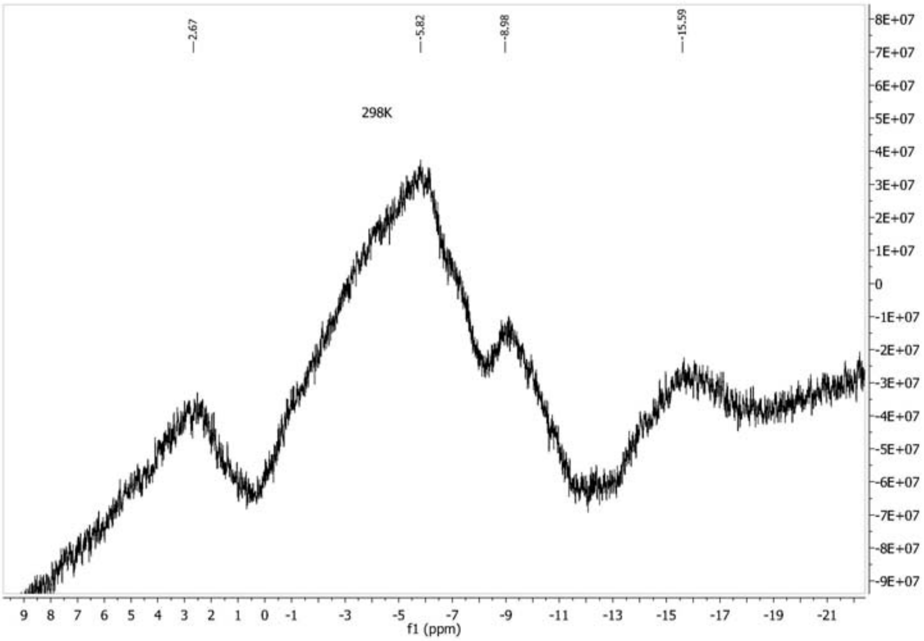
^{1}H-NMR



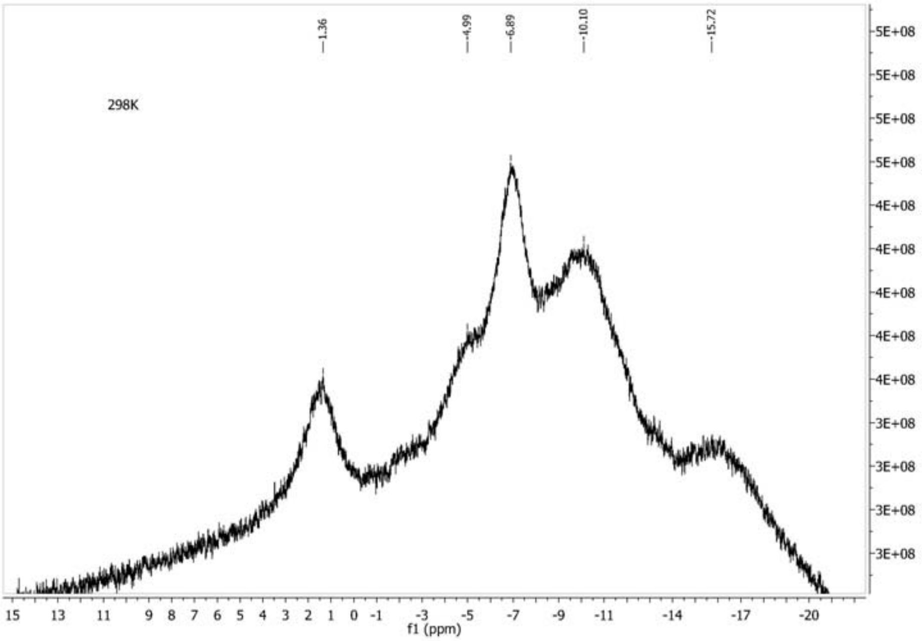
^{1}H{^{11}B}-NMR



^{11}B-NMR

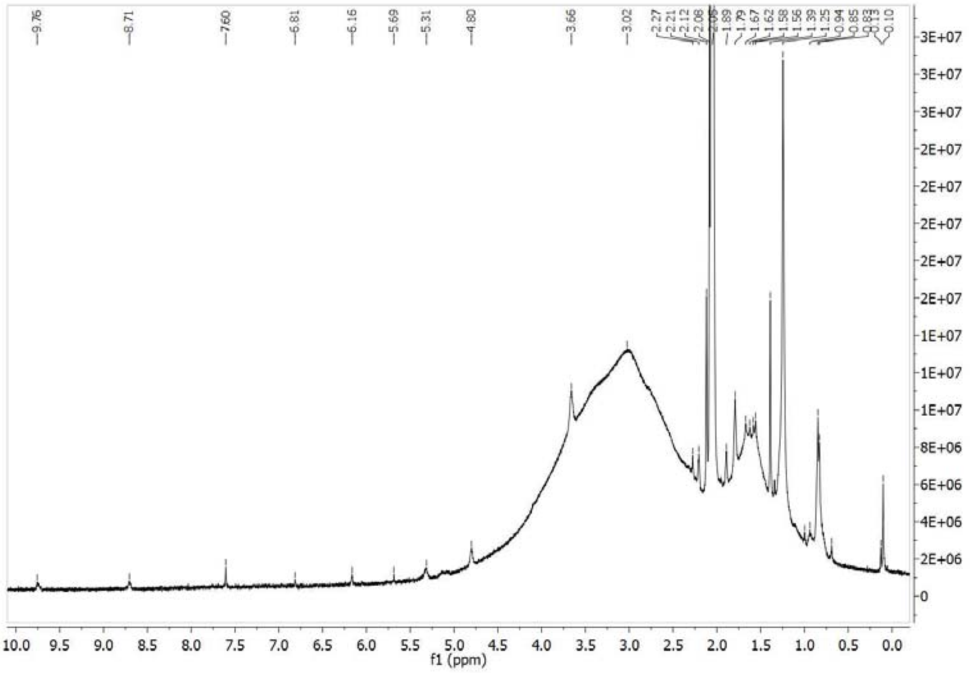


^{11}B{^{1}H}-NMR

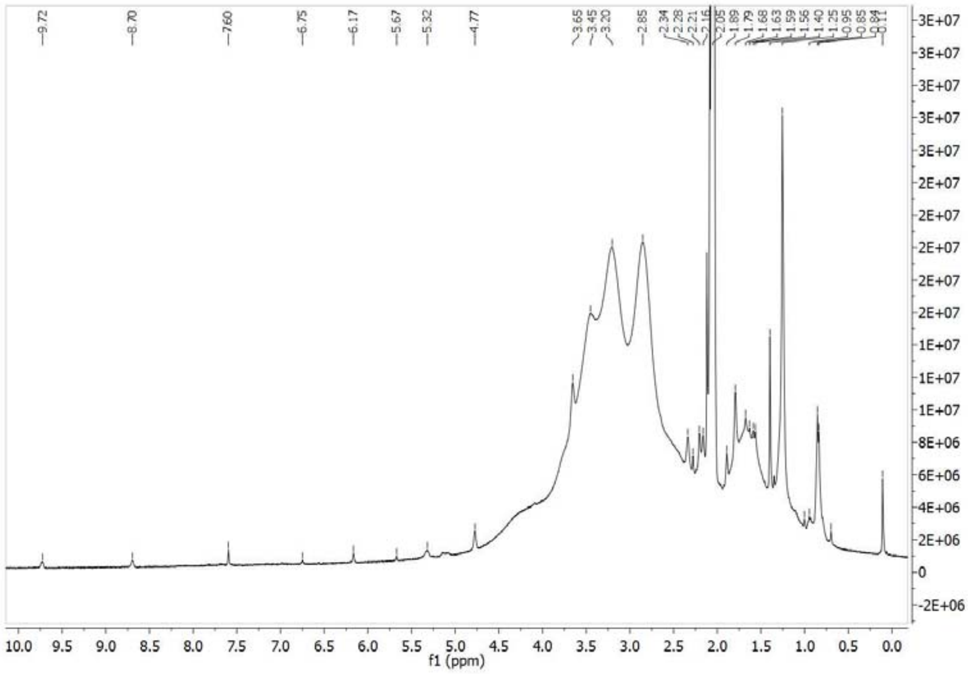


c) Compound **3**

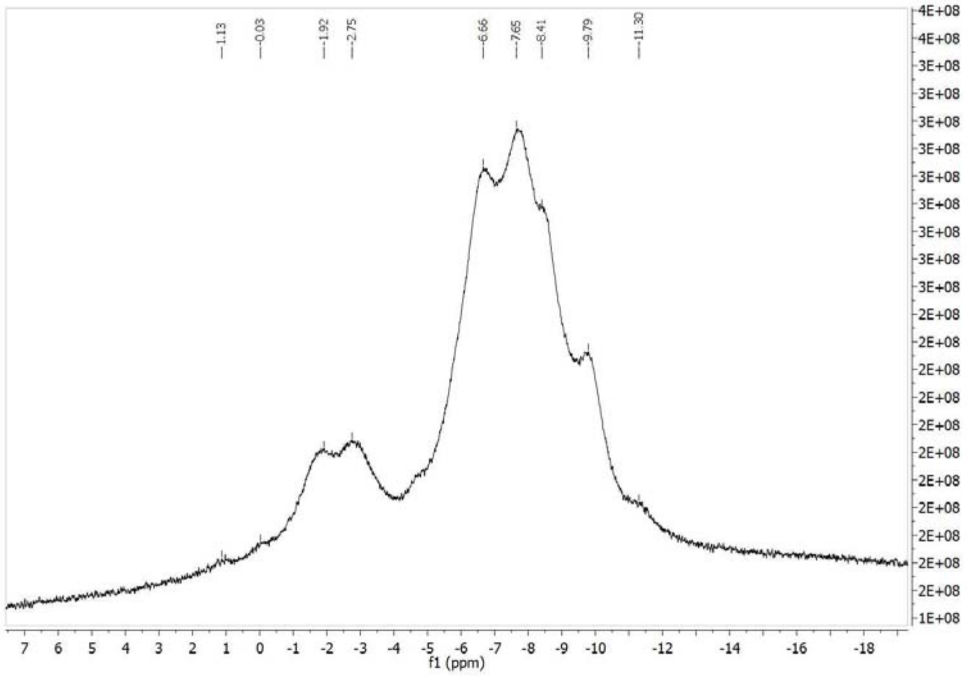
^{1}H-NMR



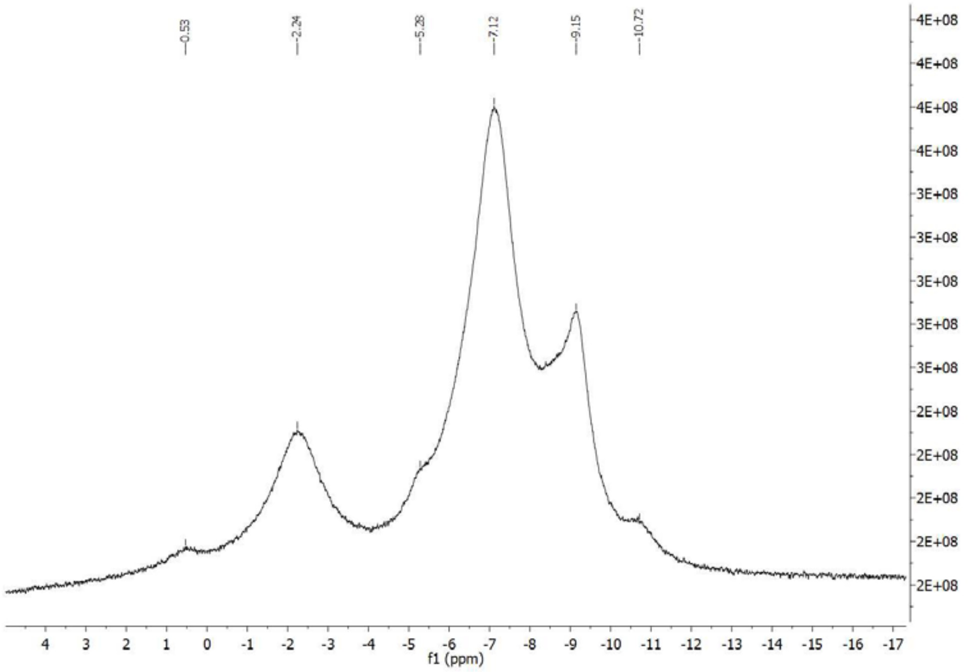
^{1}H{^{11}B}-NMR



^{11}B-NMR

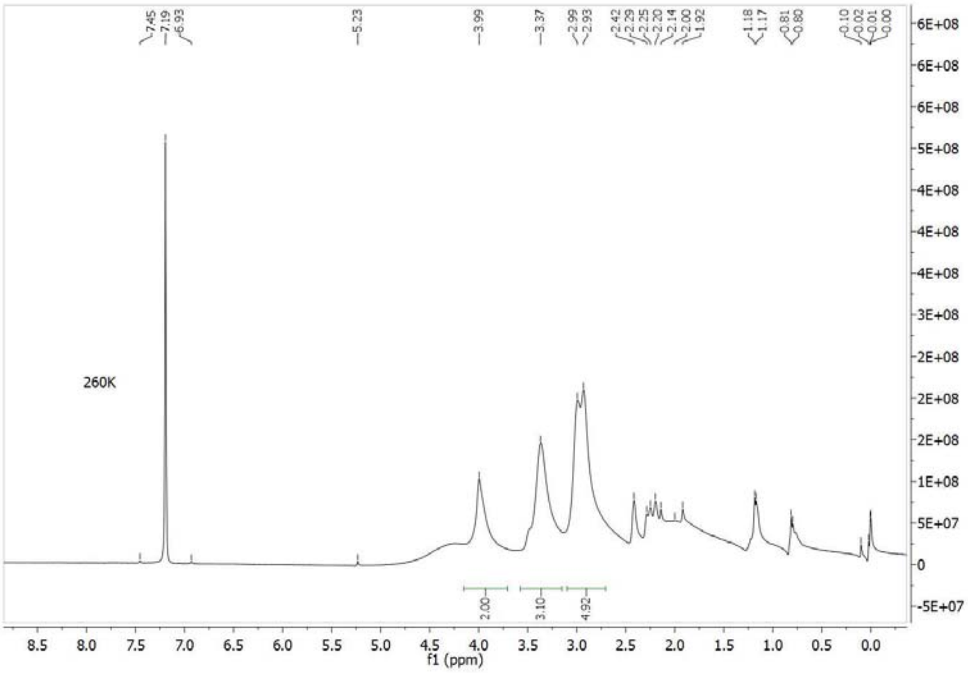


^{11}B{^{1}H}-NMR

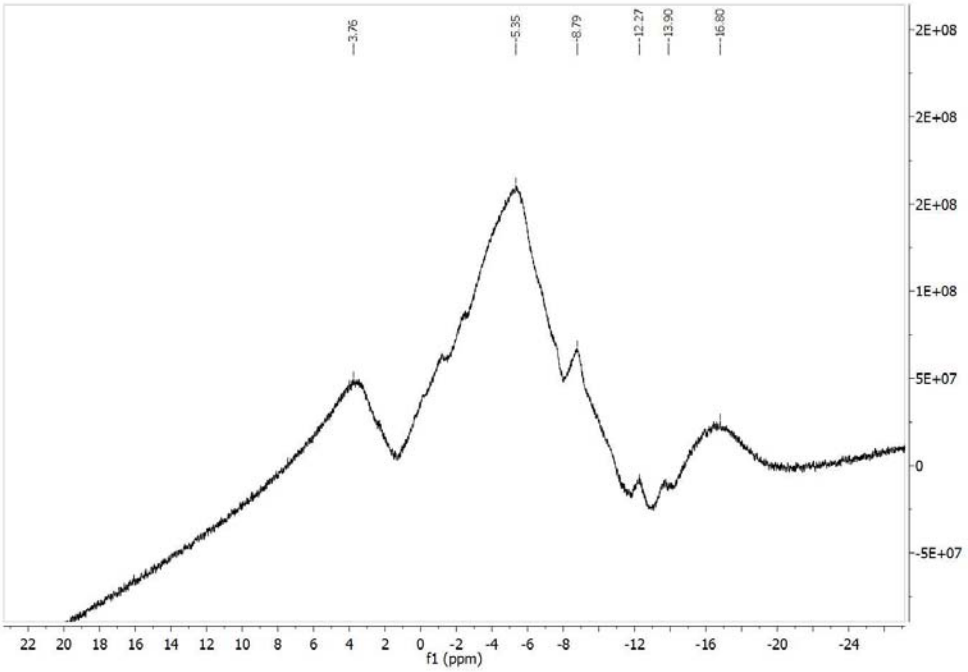


d) Compound **4**

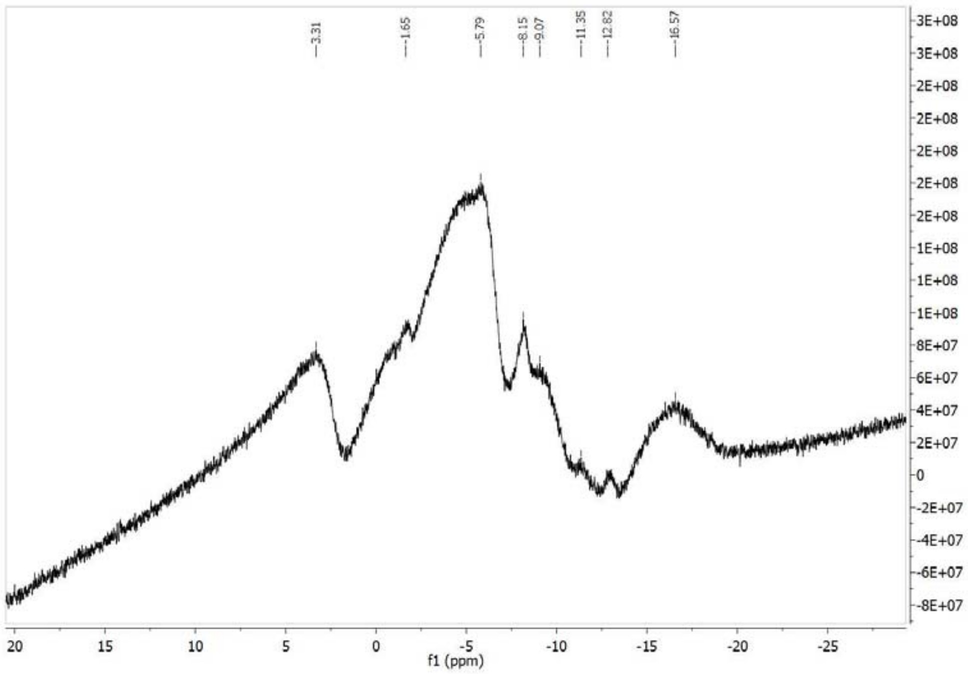
^{1}H-NMR



^{11}B-NMR



$^{11}B\{^{1}H\}$-NMR


3.31
-1.65
-5.79
-8.15
-9.07
-11.35
-12.82
-16.57
3E+08
3E+08
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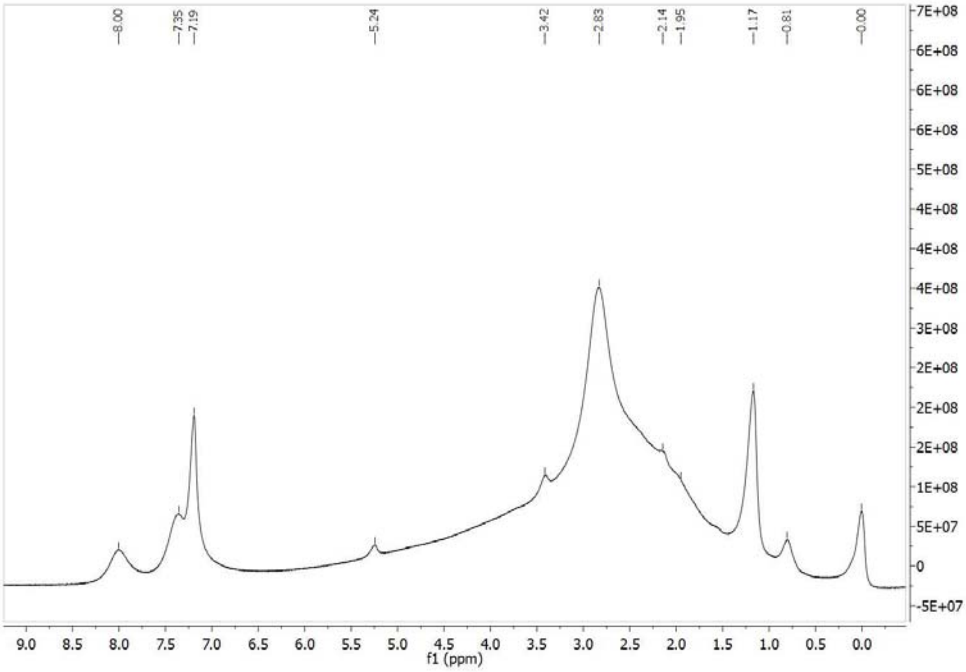
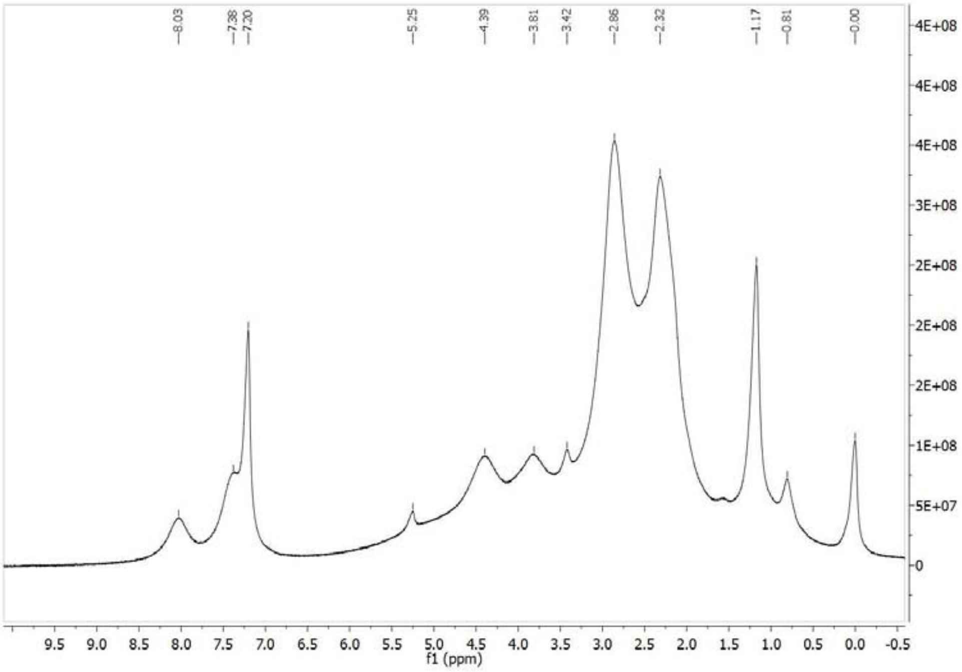
2E+08
2E+08
2E+08
2E+08
1E+08
1E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
-4E+07
-6E+07
-8E+07
20
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)

e) Compound **5**

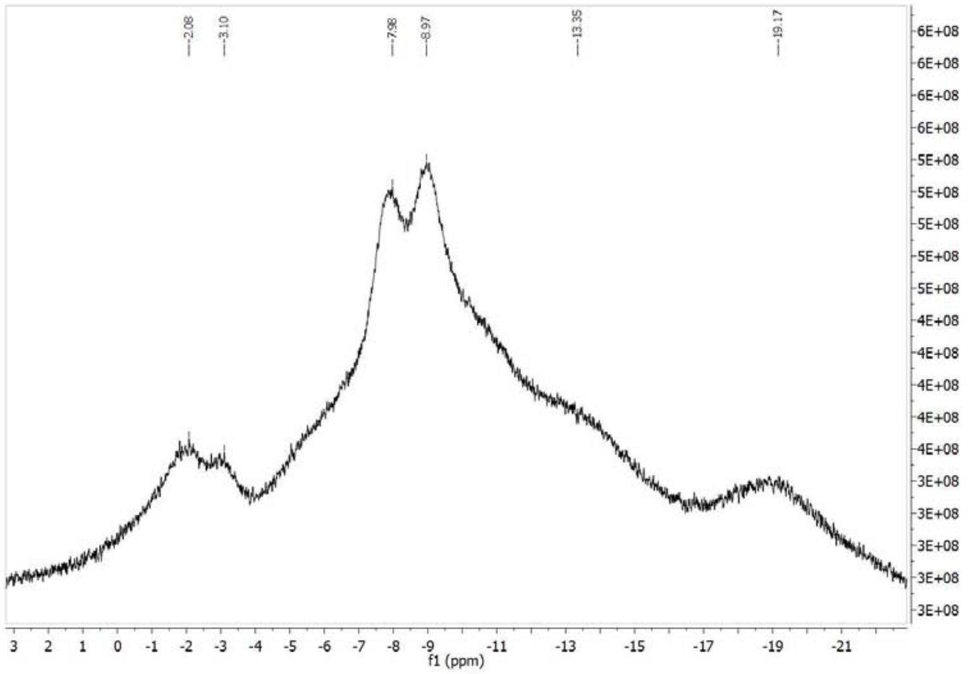
^{1}H-NMR



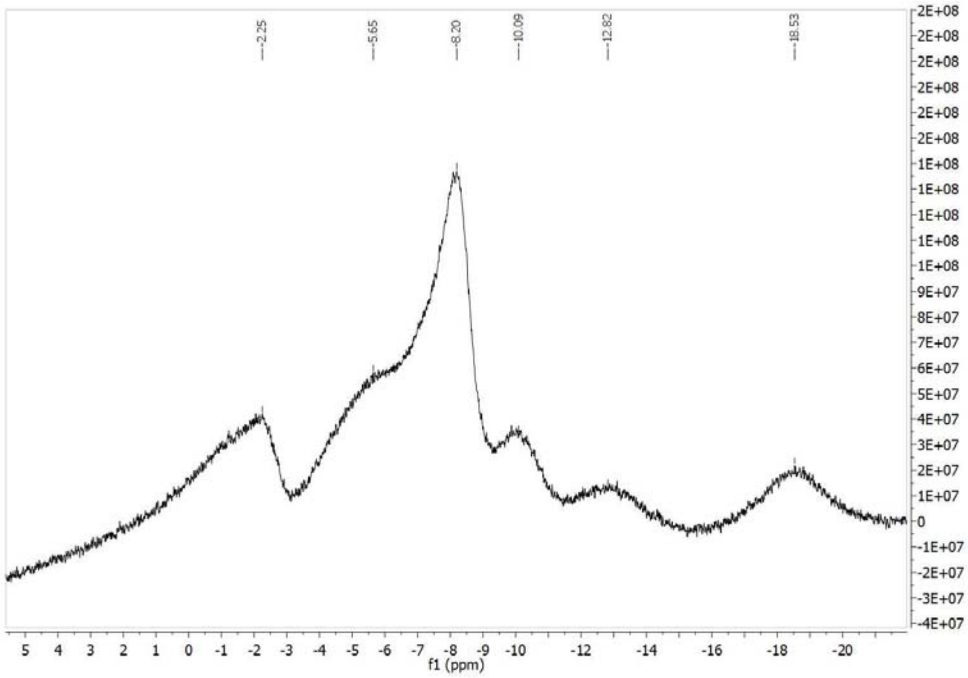
^{1}H{^{11}B}-NMR



^{11}B-NMR

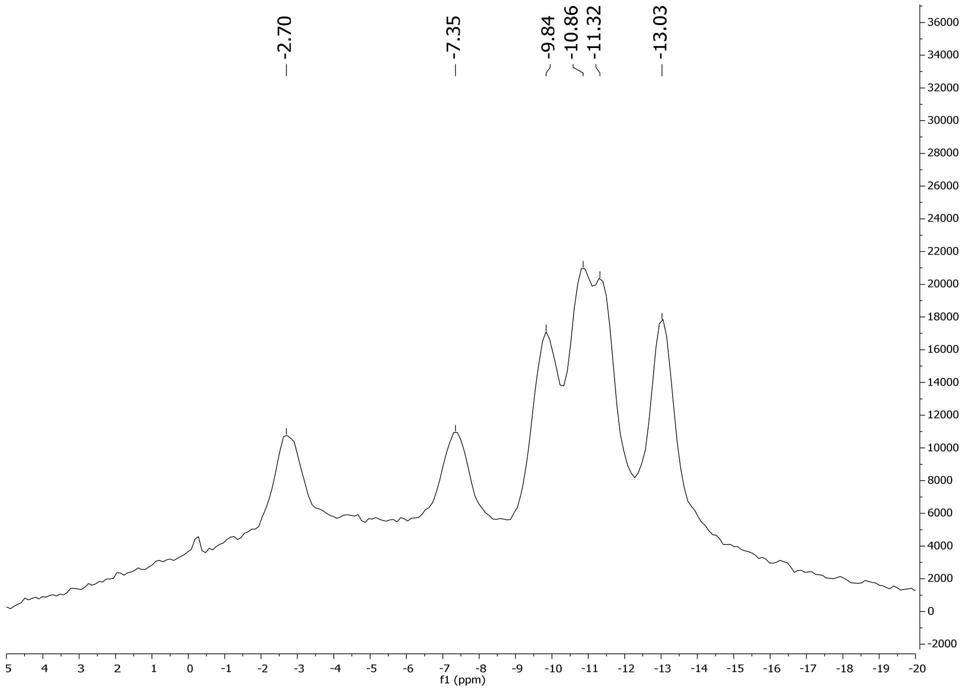


^{11}B{^{1}H}-NMR

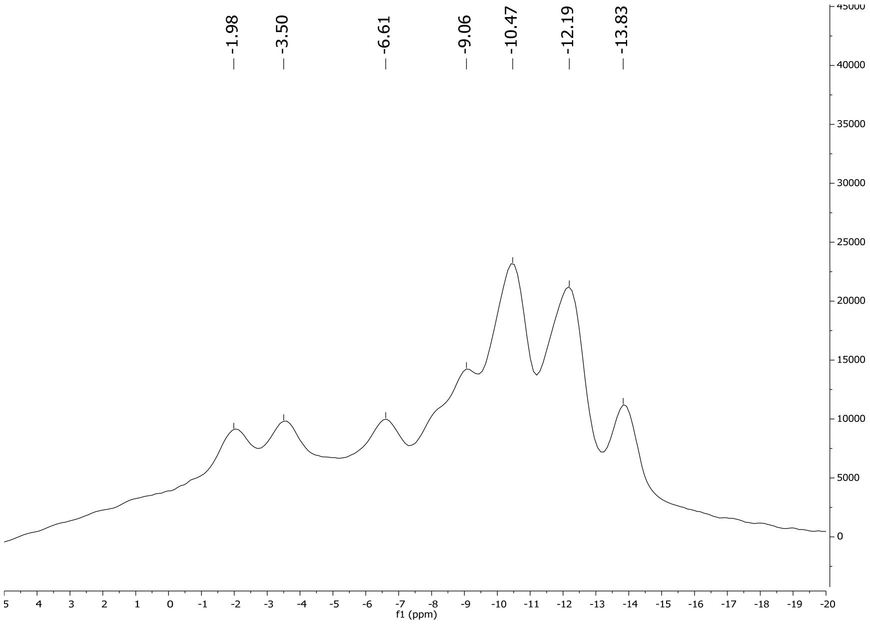


f) Ligand **LH**

^{11}B-NMR in d$_6$-acetone.



^{11}B{^{1}H}-NMR in d$_6$-acetone.



$^{13}C\{^{1}H\}$-NMR

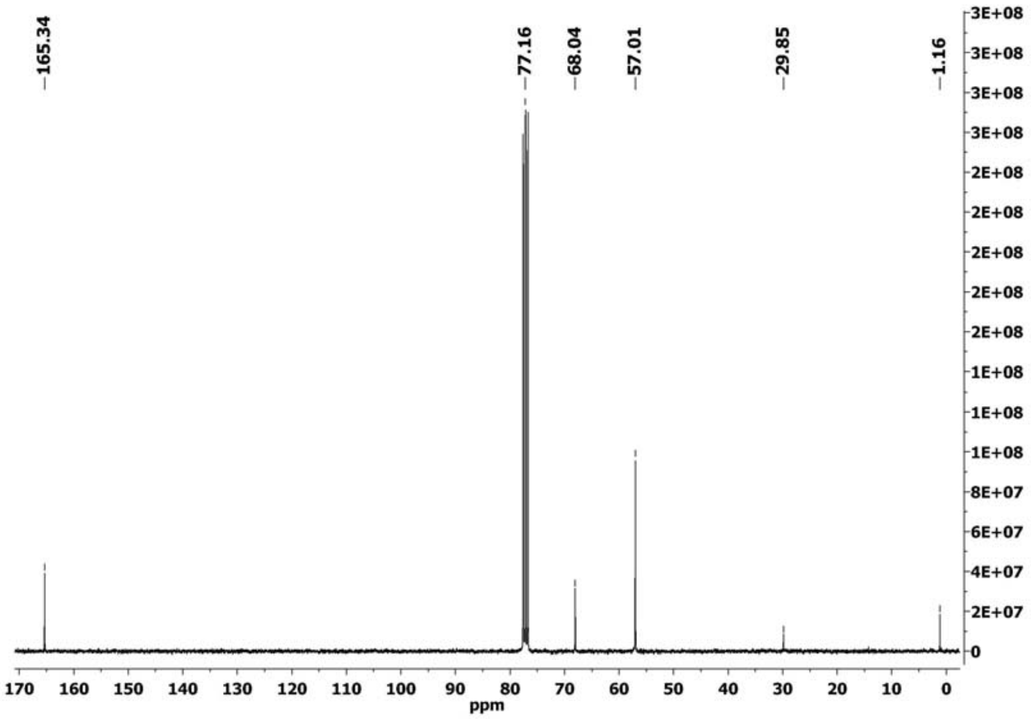
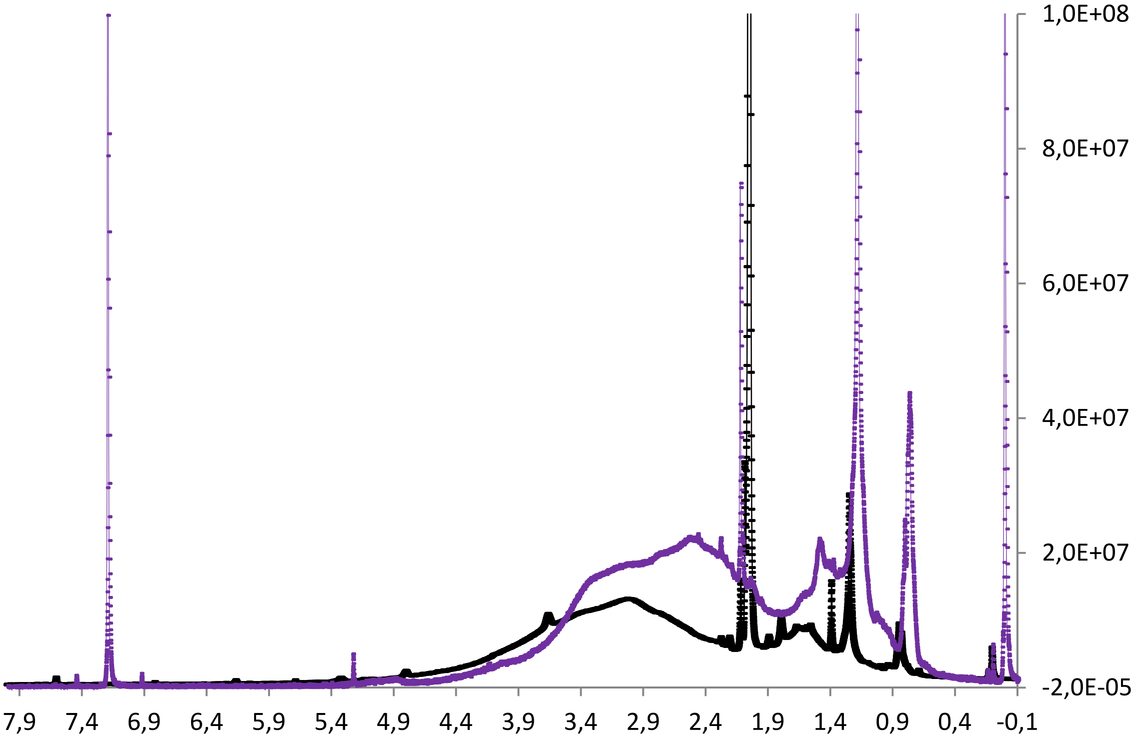

165.34
77.16
68.04
57.01
29.85
1.16
3E+08
3E+08
3E+08
3E+08
2E+08
2E+08
2E+08
2E+08
2E+08
1E+08
1E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Figure S4. Comparison of a) ^{1}H-NMR of compound **3** in chloroform (purple) and in acetone (black), b) ^{1}H{^{11}B}-NMR of compound **3** in chloroform (purple) and in acetone (black).

a)



b)

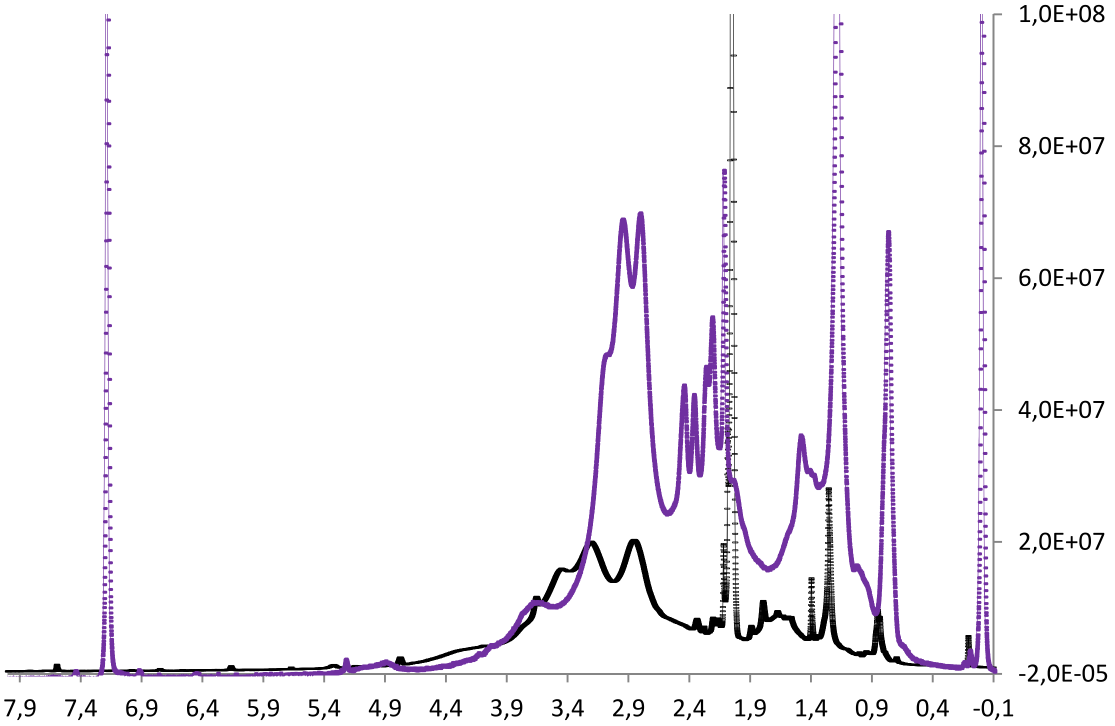


Figure S5. $^{1}H\{^{11}B\}$-NMR of compound **3** in d_6-acetone at 260K.

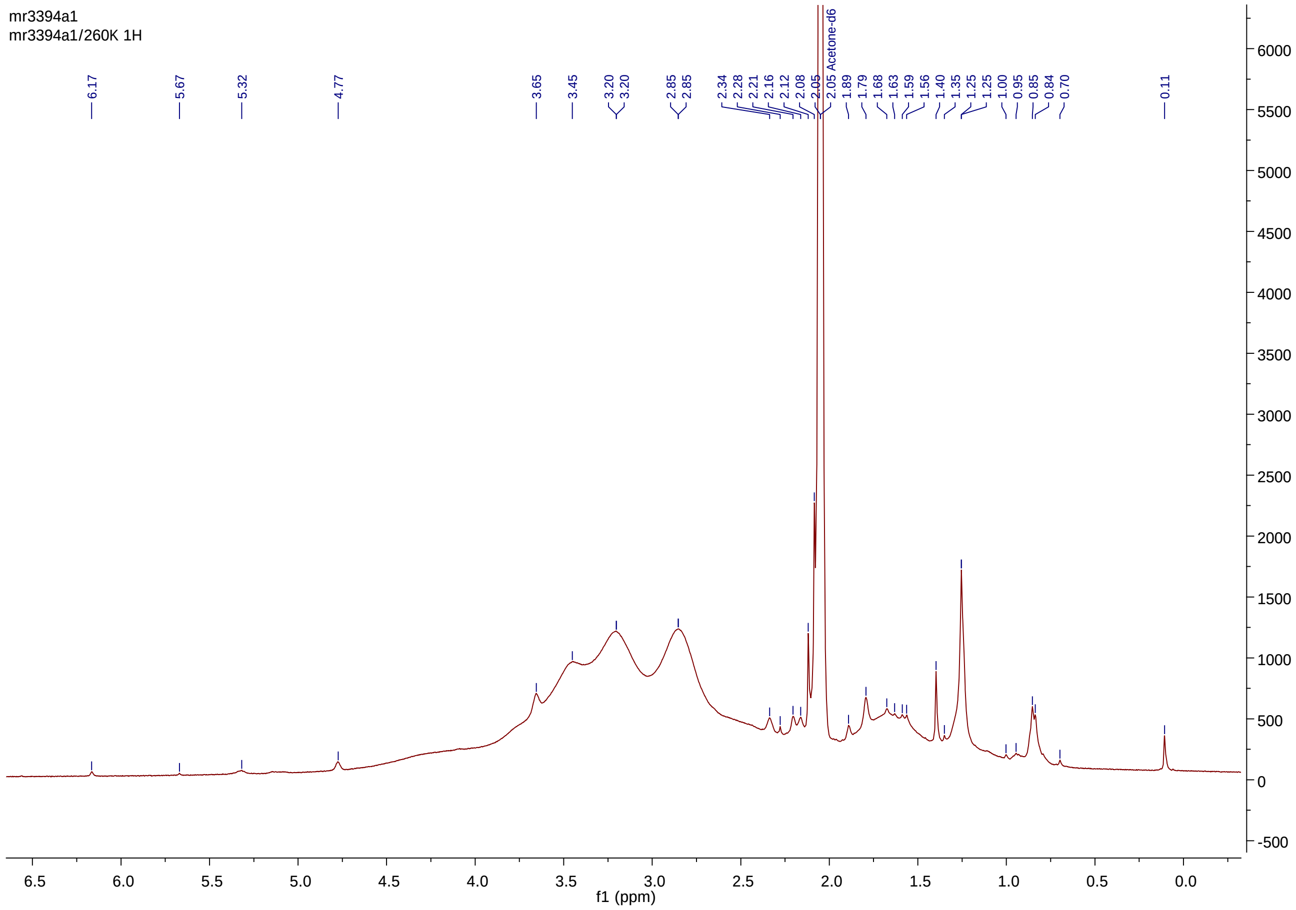


Figure S.6.- 1H{11B}-NMR and 1H-NMR of compound 3 at room Temperature.